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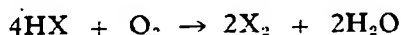
(54) OXIDATION OF HYDROGEN HALIDES USING 13X
 MOLECULAR SIEVE CATALYSTS

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in processes based on catalytic reactions involving oxidation of a hydrogen halide to release free halogen, or to halogenate organic compounds in situ. In particular, it relates to improvements in such processes wherein the catalysts employed are those wherein the alkaline, alkaline earth, or other metal ions of a 13X molecular sieve support are exchanged by metals which are active for hydrogen halide oxidation and oxyhalogenation reactions. The improved process has particular utility in fixed bed oxidation reactions with hydrogen chloride or hydrogen bromide, including particularly oxychlorination and oxybromination reactions to produce organohalides.

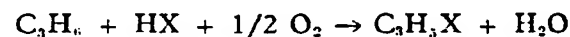
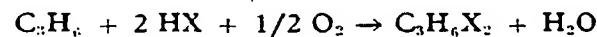
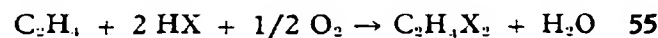
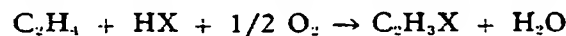
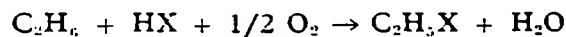
Large quantities of by-product hydrogen halides are produced by the chemical process industries, and such production is increasing annually. Present processes are ineffective in converting the hydrogen halides to the free halogen, or in effecting the in situ halogenation of organic compounds, e.g., hydrocarbons. Consequently, the generation of such products often represents waste and, worse, even creates disposal problems.

Numerous processes are described in the prior art, especially those of the Deacon type, wherein supported active metal salts are used as catalysts to convert hydrogen halide to the free form as represented, e.g., by the following equation wherein X represents halogen:



In addition, processes are known wherein a
 [Price 25p]

suitable compound, e.g., an organic compound, is introduced with the hydrogen halide and oxygen, or oxygen-containing gas, so that the compound is halogenated. In such reaction the halogen, in some form, is generated in situ, and used to halogenate the added compound. The oxyhalogenation of representative hydrocarbons can thus be illustrated as follows:



A major problem in such reactions is associated with the volatility of the metal halide salts which are used for impregnation of the supports. The metal halide salts are lost with the gases which evolve from the process. Efforts have been made to overcome this problem. For example, rare earth metal halides have been added to reduce the vapor pressure of the active metal halide deposited on the support. Also, fluidized beds have been employed to provide better heat distribution and thus prevent the formation of hot spots which aggravates the tendency toward volatilization. Such efforts, however, have been only partially successful. Higher activity and longer catalyst life are also desired. Efforts to increase activity, e.g., by addition of earths, refractory materials, porous clays and the like with the catalyst to absorb water, have been only partially successful.

The present invention uses catalysts wherein salts of metals active for oxidation of hydrogen halides or oxyhalogenation reactions are deposited or exchanged on a 13X zeolite molecular sieves in place of the alkaline, alkaline earth, or other metal ions of a molecular sieve support. The resulting cation exchanged

molecular sieves are excellent catalysts for hydrogen halide oxidation or oxyhalogenation reactions. The normal catalytic activity is enhanced, and the catalyst can be used for long periods of time. The said active metals are those of Groups IB, IIB, VB, VIB, VIIB, VIII and the rare earth metals of Group IIIB of the Periodic Table of Elements.

Catalysts suitable for the practice of this invention are formed by introducing active metals into the internal adsorption area of 13X zeolitic molecular sieves, whether natural or synthetic. Preferably, the active metals are exchanged for the inactive species of the sieve. A satisfactory method of accomplishing this is to contact the sieve intimately with an aqueous solution of a water-soluble salt of the metal to be deposited in the internal adsorption area. The metal cations or inactive species of the sieve are exchanged for those of the aqueous solution. Following this, the zeolitic molecular sieve is separated from the aqueous exchanging solution and dried. This step can be conveniently accomplished by washing the sieve with water to free it from the exchanging solution, and then drying at sufficient temperature, e.g., at about 500°F., to remove virtually all of the water.

The reason for the effectiveness of these catalysts is not known. It is believed, however, that the reactions largely take place within the internal adsorption areas of the 13X molecular sieves, the exchanged metal ion forming partial halides, in situ, as reactive intermediates which decompose to liberate elemental halogen. Whatever the mechanism, however, metals of salts of the Deacon type, such as, e.g., the halides of copper, iron, chromium, manganese, rare earth metals, and the like, when deposited or exchanged within the molecular sieves, exhibit remarkable activity and exceptional stability. In fact, the activity is enhanced as contrasted with similar metal salts deposited on conventional supports, and often the activity of a known low activity species is increased sufficiently to be considered highly active.

The 13X molecular sieves useful for the practice of this invention are, for example, those described in U.S. Patents 3,013,982 to U.S. 3,013,987. These patents also describe various methods for deposition and exchange of ions. In the expressions "13X zeolitic molecular sieves" and "13X molecular sieves" the letter "X" is used to distinguish the interatomic structure from that of other types (for example the "A" type); and the terms "zeolitic molecular sieves" or "molecular

sieves" are employed herein to mean sieves consisting of three-dimensional frameworks of SiO_2 and AlO_2 tetrahedra, cross-linked by the sharing of oxygen atoms. The terms thus exclude clays, for example montmorillonite and other bentonitic clays. The electro-valence of the tetrahedra containing aluminum is balanced by the inclusion in the crystal of a cation, e.g., an ion of an alkali, alkaline earth metal, ammonia, amine complexes or hydrogen. Such cations can be exchanged for cations known to be active for hydrogen halide oxidation or oxyhalogenation reactions by generally conventional techniques. Suitably, aqueous solutions of the salts of active metals are used to treat the 13X molecular sieves, and the inactive metal species of the sieve is thus exchanged by transition metals of Group IB metals such as copper, silver and gold; Group IIB metals such as zinc, cadmium and mercury; Group VB metals such as vanadium, niobium and tantalum; Group VIB metals such as chromium, molybdenum and tungsten; Group VIIB metals such as manganese, technetium and rhenium; Group VIII metals such as iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, and the rare earth metals of Group IIIB. In preparing the aqueous solution for ion exchange, salts of amphoteric metals can be dissolved in acidic or basic solutions, while other metal salts can be dissolved in weakly acidic solutions. The salts may also be dissolved in non-aqueous organic solvents. The salts can be used in any convenient form, e.g., as halides, sulfates, nitrates, or coordination complexes, i.e., amines or ethylene diamine tetraacetic acid salts. After completion of the exchange, the sieve is dried to remove water or other adsorbate molecules.

The activated catalyst can be used in the reactions as a fixed bed or moving bed, or can be fluidized. Use of the catalysts as fixed beds offers unique advantages inasmuch as the catalyst is non-volatile.

The invention will be better understood by reference to the following examples which present illustrative data wherein the chloride salts of copper, iron, and chromium are exchanged from acidic aqueous solution on 13X-type molecular sieves, the sodium being exchanged for these metals. These data are compared with conventional catalysts in fixed bed reactions. It is shown that the resulting cation-exchanged molecular sieves are excellent catalysts for hydrogen chloride oxidation. The catalysts last for long periods of time, and superior chlorine yields are obtained.

EXAMPLES 1—3

HYDROGEN CHLORIDE OXIDATION USING TYPICAL CATALYSTS

HCl/O₂ = 1/0.25 moles; HCl Space Velocity = 80 V/V/Hr.
 Temperature = 900°F.; Catalyst as Indicated

Example Number	Catalytic Metal Ion and Salt Used for Exchange	Percent Chlorine Yield With	
		Catalyst Metal Ion on Al ₂ O ₃ (5 m ² /g)	Catalyst Metal Ion on 13X Molecular Sieve
—	None	4.0	0
1	Cu ⁺⁺ (CuCl ₂)	50.5	69.0
2	Cr ⁺⁺⁺ (CrCl ₃)	14.5	61.0
3	Fe ⁺⁺⁺ (FeCl ₃)	12.8	64.0

In the above table, Column 2 shows the catalytic metal ion (and original salt) exchanged on the molecular sieve. Columns 3 and 4, for comparative purposes, show the chlorine yield of conventional catalysts vis-a-vis the catalysts of the present invention, respectively. Thus, in Column 3 there is shown the results obtained by use of conventional catalysts wherein the respective metal is deposited on an alumina support. In Column 4 there is shown the results obtained wherein the metal is ion-exchanged with a 13X-type molecular sieve. In all instances, as will be observed, the yield of chlorine in the latter instance is far superior to the yield obtained when utilizing conventional catalysts. In fact, the activity of catalyst which is normally low exceeds that of catalysts which are normally very high.

EXAMPLE 4

In the following example, a typical catalyst preparation is described and comparative data

are given to demonstrate the improved catalyst life obtained by virtue of the ion-exchange catalyst.

Fifty grams cupric chloride is dissolved in 200 ml. of distilled water, and to this solution is added a solution of ammonium hydroxide which completely converts the cupric (Cu⁺⁺) ion to the cupra-amine complex ion. One hundred grams of dry, molecular sieve 13-X (sodium form) is then added to the above amine complex solution, the solution is heated to 60°C. and the mixture stirred for 30 minutes. After this time it is allowed to stand and the supernatant solution drained. The exchanged sieve is then washed with distilled water until free of the copper ion. All washings are collected, and analyzed for Cu⁺⁺, Na⁺ and Cl⁻ ions to determine the amount of copper ion exchange. The sieve is dried at 500°F. for 4 hours. The catalyst is then used in a fixed bed hydrogen chloride oxidation reaction, as tabulated below:

CATALYST LIFE IN HYDROGEN CHLORIDE OXIDATION

HCl/O₂ = 1/0.25 Moles
Temperature = 800°F.

Percent Chlorine Yield with

Time on Feed, Hours	CuCl ₂ on Al ₂ O ₃	Cu ⁺⁺ on Molecular Sieve 13X (Linde)*
1	50.5	72.5
4	8.4 ⁽¹⁾	69.5
17	—	73.0

⁽¹⁾ At the end of four hours all the CuCl₂ had sublimed away from the alumina base; hence, the very poor yield.

*"LINDE" is a registered Trade Mark.

EXAMPLE 5

The use of cation-exchanged molecular sieves in the oxyhalogenation of hydrocarbons is conveniently illustrated by the following example:

Ethylene, hydrogen chloride and oxygen in mole ratios of 1/3/0.6 are passed over a Cu-exchanged molecular sieve catalyst as employed in Example 4, in fixed bed, at 800°F. A 61 percent ethylene conversion is obtained with a 61.3 percent selectivity to vinyl chloride.

The present invention is particularly useful for the oxidation of hydrogen chloride and hydrogen bromide, and the catalyst has particular utility in fixed bed reactions. It is also particularly useful for the halogenation of hydrocarbons such as paraffins, for example, methane, ethane, propane, pentane, heptane and hexane; aliphatically unsaturated compounds, for example, ethylene, propylene, 2-butene, 2-methyl-1-butene, 3-hexene, 4-methyl-3-heptene, 4-methyl-4-octene, 2-butyl-1-octene, 1,3-butadiene, 2,3-hexadiene, 1,2-heptadiene, 3-methyl-1,5-octadiene, acetylene, methacetylene and cyclobutylene; and aromatic compounds, e.g., benzene, toluene and propyl benzene.

Suitable oxidizing agents are oxygen, air, ozone, or other oxygen-containing gases. The mole ratio of oxygen-to-halide generally employed ranges from 0.1:1 to 3:1, and preferably from 0.2:1 to 1:1.

Inert gas diluents, such as nitrogen, helium, and argon, can also be used in the reaction. The mole ratio of diluent-to-oxygen generally employed ranges from 10:1 to 0.5:1 and preferably 5:1 to 1:1, or more preferably 4:1.

Space velocities based on the hydrogen halide employed in the reaction range between 500 to 10 V/V/Hr., and preferably from 200 to 50 V/V/Hr., or more preferably from 150 to 100 V/V/Hr.

Temperatures for the reactions generally range up to 1500°F., and preferably range from 500°F. to 1000°F. Pressures range generally from atmospheric to 250 psig, and preferably up to 150 psig. Temperature and pressure, however, are largely determined by the nature of the particular reactions.

The 13X molecular sieves most useful in the practice of this invention are readily ion exchanged in a weakly acidic or basic aqueous solution. For example, the desired 13X molecular sieve can simply be charged into a vertical vessel and eluted with the appropriate metal ion solution to exchange the latter for sodium, followed by repeated washings with distilled water. The ion-exchanged sieve is then heat dried to remove water.

The active metal can also be deposited in the molecular sieve by ion exchange with organic solvent soluble salts of the active metal, or organic solvent soluble metal complexes of the active metal.

WHAT WE CLAIM IS:—

1. A process for producing a halogen, wherein a hydrogen halide and oxygen are contacted together and reacted in the presence of an active catalyst which is a 13X molecular sieve and in which is deposited or exchanged a metal selected from one of the Groups IB, IIB, VB, VIB, VIIB, VIII and the rare earth metals of Group IIIB, of the Periodic Table of the Elements.

2. The process of Claim 1, wherein an oxygen-containing gas and a hydrogen halide are reacted in the presence of a hydrocarbon compound under conditions whereby the latter is halogenated.

3. The process of Claim 1 or 2, wherein the metal is deposited within the molecular sieve by ion exchange with a water-soluble salt of the said metal.

4. The process of Claim 1 or 2 wherein the metal is deposited within the molecular sieve by ion exchange with a non-aqueous organic solvent-soluble salt of the said metal.
- 5 5. The process of Claim 1 or 2, wherein the catalyst is formed by contact of the molecular sieve with a solution of a water-soluble, or non-aqueous organic solvent-soluble, metal complex of the said metal, and the sieve then
- 10 dried to obtain an active catalyst.
6. The process of any of Claim 1 to 5, wherein the oxidized hydrogen halide is hydrogen chloride or hydrogen bromide.
- 15 7. The process of any of Claims 1 to 6, wherein the reaction is conducted with a fixed bed of catalyst.
8. The process of any preceding claim, wherein the metal is copper, iron or chromium.
9. The process of any preceding claim, wherein the reaction is conducted at a temperature in the range 500°F to 1000°F, and at a pressure in the range atmospheric to 250 p.s.i.g.
- 20 10. The processes according to claims 1 and 2 of oxidation of hydrogen halides and oxyhalogenation of organic compounds, substantially as herein described.
- 25 11. The processes according to claims 1 and 2, substantially as described herein with reference to any one of the Examples.
- 30 12. Halogens and organic oxyhalogenation products when obtained by a process claimed in any preceding claim.

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